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(71) Applicant *(for all designated States except US)*: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)* : JACKISCH, David, Allan [US/US]; 307 Walden Road, Wilmington, DE 19803 (US).

(74) Agents: COSTELLO, James, A. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

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(57) Abstract

A tablet formulation comprising a pesticide and a delivery system, the delivery system comprising a range of acid/base combinations, a dispersant, a wetting agent, polyvinylpolypyrrolidone, and a characterizing internal desiccant to ensure tablet stability, the tablet being selected to complement the particular class of base selected for the formulation.

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TITLE

TABLET FORMULATION WITH INTERNAL DESICCANT

An effervescent tablet produces gas bubbles by the reaction between an acid and a base. Should the water level in the tablet exceed about 0.1%, the tablet will begin to lose its effervescence even though it is stored in its container. Normally, an amount of water exceeding 0.1% is required to formulate a tablet having acceptable integrity and strength.

One way to keep the water employed during formulation from ruining the tablet during long-term storage is to package the tablet with a desiccant. The water in the tablet diffuses out and is taken up by the desiccant. This water is held by the desiccant and so cannot cause the acid/base reaction to occur. However, the need for an external desiccant complicates design of the tablet package.

One such tablet formulation that does not have an internal desiccant is disclosed in WO 90/00007. Two formulations that contain an internal desiccant are disclosed in CA-A-2,013,918 and WO 88/09161. CA-A-2,013,918 discloses a tablet comprising potassium carbonate and/or potassium bicarbonate as bases and a desiccant which physically adsorbs water. WO 88/09161 discloses an effervescent tablet for cleaning dentures comprising pancreatin, an acid component, a base component, and a drying agent.

SUMMARY OF THE INVENTION

This invention comprises a tablet formulation consisting essentially of by total weight of the formulated composition:

(i) about 0.1% to 75% of a pesticide;

(ii) about 25% to 99.9% of a delivery system characterized by a panel of components complementary to the pesticide of (i) having the following components:

(a) about 5% to 75% of a dibasic or tribasic organic carboxylic acid or a mixture thereof;

(b) about 5% to 75% of an ammonium, lithium, sodium or potassium carbonate or bicarbonate or a mixture thereof;

(c) about 0.5% to 20% of a dispersant;

(d) about 0.1% to 5% of water-insoluble cross-linked polyvinyl-polypyrrolidone;

(e) about 0.1% to 5% of an anionic or nonionic wetting agent; and

(f) about 1% to 20% of an internal desiccant being selected from the group:

(A) one or a mixture of desiccants that chemically bind water, and

(B) one or a mixture of desiccants that physically adsorb water;

the desiccant being (A) when (b) is potassium carbonate or potassium bicarbonate.

This delivery system is characterized by the inter-relationship of components (a) to (f) in the recited ranges to effect rapid disintegration of finely dispersed pesticide particles (i). Preferred ranges of the composition are 5% to 70%, more preferably 10% to 60% of the pesticide; and 30% to 95%, more preferably 40% to 90% of the delivery system.

By "tablet formulation" is meant the tablet made from the composition described herein, as well as the composition formulated in accordance with this disclosure but not in tablet form. The preferred tablet formulation of the present invention is in the form of a tablet.

Contemplated pesticides include those selected from the following classes, including mixtures thereof: herbicides, fungicides, bactericides, insecticides, nematocides, acaricides, and growth regulants.

Preferred dibasic and tribasic organic carboxylic acids include citric, fumaric, phthalic, maleic, malic, oxalic, adipic, glutaric, 2-methyl glutaric, succinic, and tartaric, or mixtures of any of them.

The term "dispersants" includes sodium, potassium, ammonium and calcium salts of naphthalene sulfonic acid-formaldehyde condensates; lithium, sodium, potassium, calcium, and ammonium salts of lignosulfonates; sodium; potassium and ammonium salts of polyacrylates and carboxylates; sodium salts of maleic anhydride-isobutylene copolymers; and water soluble nonionic polymers such as polyvinyl-pyrrolidone, polyethylene oxides and cellulose derivatives. Preferred dispersants include the sodium, potassium, ammonium and calcium salts of naphthalene sulfonic acid-formaldehyde condensates, with the ammonium salts more preferred.

Water-insoluble, cross-linked polyvinylpolypyrrolidone disintegrant refers to any of the generic, but is not limited to, crospovidone disintegrating agents.

The term "anionic wetting agent" includes, but is not limited to, salts of alkylbenzene sulfonates, alkyl and dialkylnaphthalene sulfonates, alkyl and

alcohol sulfates, sulfoalkylamides, carboxylates, alpha-olefin sulfonates and dialkyl sulfosuccinates. The term "nonionic wetting agent" includes acetylenic diols, ethylene oxide-propylene oxide copolymers, alkylphenol ethoxylates, fatty acid ethoxylates, alcohol ethoxylates, sorbitan fatty acid ester ethoxylates and castor oil ethoxylates. The preferred wetting agents are sodium dialkyl sulfosuccinates of which sodium diisobutyl sulfosuccinate, sodium diamyl sulfosuccinate and sodium dicyclohexyl sulfosuccinate are more preferred.

The internal desiccants that "chemically bind" water are those that actually undergo chemical reactions with water to form a new compound. An example of this type of material is CaO which reacts with water to form $Ca(OH)_2$. Other materials representative of those which react in this manner are magnesium oxide and boric anhydride.

The internal desiccants that "physically adsorb" water are those selected from the group consisting of highly-dispersed silicilic acids such as silica gel; aluminum oxide; clays such as montmorillonite; and amorphous and crystalline aluminosilicates such as molecular sieves and zeolites. Combinations of these desiccants with those that form hydroxides and hydrates can be used. Kirk-Othmer's Encyclopedia of Chemical Technology (3rd ed., Vol. 8, p 115) describes desiccants suitable for use in the tablet formulation of this invention as Type 1 and Type 4 desiccants. Either type can be employed, singly or in combination, as long as the desiccant does not expand when it picks-up water. Such expansion causes the tablet to crack or crumble on long term storage.

Internal desiccants useful in the tablet formulation of this invention also include materials that chemically bind water, not in the sense of a chemical reaction that forms a hydroxide, but in the sense of a chemical reaction that produces a hydrate. Representative of useful desiccants that form hydrates are $CaSO_4$, NaOAc, $MgSO_4$, Na_2SO_4, $CaCl_2$, and $ZnSO_4$. Representative of the hydrate-forming reaction is that undergone by $CaCl_2$ to form $CaCl_2 \cdot H_2O$. One or more desiccants from each group, the hydroxide-forming and the hydrate-forming, can be employed, alone or in combination, depending on the particular properties sought by the formulator. In any event, the desiccants employed in the tablets of this invention are not those of the water-adsorbing type employed in prior art tablet formulations. Kirk-Othmer's Encyclopedia of Chemical Technology (Third Edition, Vol. 8, page 115) further describes desiccants of the type contemplated for this invention as so-called Type 1 materials.

A preferred tablet formulation is one wherein component (b) is an ammonium, sodium or lithium carbonate or bicarbonate or mixture thereof, and the internal desiccant is selected from (A), (B) and a mixture of (A) and (B).

Also preferred is a tablet formulation wherein (b) is potassium carbonate or bicarbonate or mixture thereof, and the internal desiccant is (A).

Preferred pesticides are those having a melting point of at least about 100°C and solubility in pH 7 water at 20°C of no more than about 5% by weight. Representatives of such pesticides are herbicides such as: acifluorfen, asulam, atrazine, bensulfuron, bentazon, bromacil, bromoxynil, chloramben, chlorimuron ethyl, chloroxuron, chlorsulfuron, chlortoluron, clomazone, cyanazine, dazomet, desmediphan, dicamba, dichlobenil, dichlorprop, diphenamid, dipropetryn, diuron, thiameturon, 2-[[[[*N*-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-*N*-methylamino]carbonyl]amino]sulfonyl]benzoic acid, methyl ester, fenac, fenuron, fluometuron, fluridone, fomesafen, glyphosate, hexazinone,imazamethabenz, imazaquin, imazethapyr, ioxynil, isoproturon, isouron, isoxaben, karbutilate, lenacil, MCPA, MCPB, mefluidide, methabenzthiazuron, methazole, metribuzin, metsulfuron methyl, monuron, naptalam, neburon, nitralin, norflurazon, oryzalin, perfluidone, phenmedipham, picloram, prometryn, pronamide, propazine, pyrazon, siduron, simazine, sulfometuron methyl, tebuthiuron, terbacil, terbuthylazine, terbutryn, triclopyr, 2,4-D, 2,4-DB, triasulfuron, primisulfuron, 2-/3-(4,6-bis(difluoromethoxy)pyrimidin-2-yl)ureidosulfonyl)benzoic acid methyl ester, 5-pyrazolesulfonamide, *N*-[(4-methoxy-6-methyl-pyrimidine-2-yl)-amino-carbonyl]-4-methoxy-carbonyl-1-methyl-], *N*-[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide, 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N*,*N*-dimethyl-3-pyridine-carboxamide, methyl 2-[[[[[4-ethoxy-6-(methylamino)-1,3,5-triazin-2-yl]-amino]carbonyl]amino]sulfonyl]benzoate, methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridine-carboxylate, 2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide, methyl 2-[[[[[4-(dimethyl-amino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-yl]amino]carbonyl]sulfonyl]-3-methyl-benzoate, sodium 2-chloro-6-[(4,6-dimethoxy-2-pyrimidinyl)thio]benzoate; fungicides such as: carbendazim, thiuram, dodine, chloroneb, cymoxanil, captan, folpet, thiophanatemethyl, thiabendazole, chlorothalonil, dichloran, captafol, iprodione, vinclozolin, kasugamycin, triadimenol, flutriafol, flusilazol,

hexaconazole or fenarimol; bactericides such as oxytetracycline dihydrate; acaricides such as: hexathiazox, oxythioquinox, dienochlor or cyhexatin; insecticides such as: carbofuran, carbaryl, thiodicarb or deltamethrin.

More preferred pesticides are hexazinone, 2,4-D, chlorsulfuron, sulfometuron methyl, chlorimuron ethyl, metsulfuron methyl, ethametsulfuron methyl, thifensulfuron methyl, tribenuron ethyl, bensulfuron methyl, primisulfuron, methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-6-(trifluoro-methyl)-3-pyridinecarboxylate, 2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide, ethyl 5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1*H*-pyrazole-4-carboxylate, *N*-[[(4,6-dimethoxy-2-pyrimidinylamino]-carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide, 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N*,*N*-dimethyl-3-pyridine-carboxamide, methyl 2-[[[[[4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-yl]amino]carbonyl]sulfonyl]-3-methylbenzoate, and sodium 2-chloro-6-[(4,6-dimethoxy-2-pyrimidinyl)thio]benzoate.

The most preferred pesticides are sulfonylurea herbicides such as chlorsulfuron, sulfometuron methyl, chlorimuron ethyl, metsulfuron methyl, ethametsulfuron methyl, thifensulfuron methyl, tribenuron ethyl, bensulfuron methyl, primisulfuron, methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl]-6-(trifluoromethyl)-3-pyridinecarboxylate, 2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzenesulfonamide, ethyl 5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl]-1-methyl-1*H*-pyrazole-4-carboxylate, *N*-[[(4,6-dimethoxy-2-pyrimidinylamino]carbonyl]-3-(ethylsulfonyl)-2-pyridine-sulfonamide, 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]-sulfonyl]-*N*,*N*-dimethyl-3-pyridinecarboxamide, and methyl 2-[[[[[4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-yl]amino]carbonyl]-sulfonyl]-3-methylbenzoate.

DETAILS OF THE INVENTION

The most common method for applying water insoluble pesticides is as fine aqueous dispersions which are sprayed onto the field or crop using ground or aerial spray rigs. The tablets of this invention combine a high level of physical integrity with rapid break-up in water using minimal or no agitation while providing fine dispersions of active ingredient. Since the spray nozzles are

typically protected against clogging by 50 mesh screens (U.S. mesh size), the dispersions must be fine enough to pass through this size screen without plugging it. This ability is characteristic of pesticide dispersions delivered by the delivery system of this invention.

High physical integrity of the tablets is desirable so that the tablets themselves can withstand the tabletting operation and survive handling, packaging and shipping without breaking. An axial breaking strength of greater than about $9x10^3$ newtons is generally necessary for a tablet to survive such treatment.

Rapid break-up in water is desirable for the convenience of the growers who require quick turnaround times for the preparation of the dispersions. Generally, the tablets of the invention disperse completely in less than 10 minutes, most in less than 5 minutes using even the cold water drawn from wells in the early spring.

It is substantially impossible to obtain rapid break-up of a tablet of substantially water-insoluble active ingredient in aqueous media without the use of effervescence. The reaction of the organic acid and carbonate or bicarbonate base affords carbon dioxide gas which aids in this respect.

A dispersant is required so that the particles of the active ingredient formed during the disintegration of the tablet remain separated in the cold, hard water.

The disintegrant allows the penetration of the water into the interior of the tablet through a wicking or swelling action. Common starch or cellulose-based disintegrants are unsuitable in agricultural applications as they typically form gels on the 50 mesh spray nozzle screens. Hence, a water insoluble cross-linked polyvinylpolypyrrolidone is used.

A wetting agent is required to control the size of the carbon dioxide bubbles formed during the reaction of the acid base. The wetting agent reduces the surface tension between the bubbles and the solid tablet resulting in the formation of smaller bubbles which readily detach from the tablet surface. As a consequence, the tablet remains submerged in the water for a longer period of time, thus improving contact of the entire tablet surface with water.

If a tablet floats immediately after being dropped in the water its top rapidly dries out and the reaction slows down there. This increases the time required for complete dispersion of active ingredient. When a tablet sinks, water wets the entire exterior of the tablet. Then, when the tablet floats to the surface (as a result of the buoyancy of the attached carbon dioxide bubbles when the tablet has

partially dispersed and become lighter) the top remains wet so that effervescent reaction continues. Dispersion times for active ingredients formulated as described herein are very much more rapid than in formulations that produce tablets designed for flotation. To ensure that the tablet will sink initially, inert ingredients are employed that produce a tablet with a density greater than that of water (specific gravity greater than 1.00).

Inert ingredients up to 99.9% of the total weight of the composition can be employed. Inert fillers such as sugar or clay can be added as long as they do not affect the chemical stability of the active ingredient(s). Materials such as glidants, anti-adherents, and lubricants can also be employed to facilitate production in the tablet press. The amounts and types of such ingredients will be readily determinable by one skilled in the tabletting art given the disclosure herein.

The formulation ingredients are typically ground and mixed in a mill, e.g., an air or hammermill. The ground premix is passed through a 50 or 100 mesh (U.S.A. Standard Sieve Series) screen. The average particle size of the ground premix should be in the range of 5 to 15 microns. If it is much smaller, the tablet will be strong, but will not break up very fast. If the premix is much larger, the dispersion will not be fine enough to pass a wet screen test used to indicate whether the dispersion will clog the spray nozzle and protective screen discussed previously.

The tablets can be prepared using conventional tablet-making equipment. Their diameter can vary from about 1 cm or less, to 7.5 cm, depending on the tablet weight desired. Flat-faced, beveled-edge punches, with or without a breakline, product attractive tablets.

To keep the tablet from sticking to the die or punch faces, a lubricant such as magnesium stearate or boric acid can be used. Such lubricants and anti-adherents can be brushed onto the die surface or incorporated into the formulation.

Tablets have been formed in a hydraulic press with a capacity of 18,000 kg of force. Pressures between about 3.43×10^7 to 6.86×10^7 pascals will produce strong tablets that break up rapidly. Break-up times are determined by dropping a tablet, typically 5 to 15 g into 1000 mL of water. The "end point" of final dispersion is easy to determine because the tablet floats to the surface as it loses weight shortly before it finally disperses.

The resultant dispersion is then poured through a nest of 50/100/200 mesh screens (300 mm, 150 mm, 75 mm holes, respectively). A qualitative judgment is then made about the amount of material that is retained on each screen. A good tablet will leave just a "trace" on the 200 mesh screen, and the larger screens will be free of residue.

The strength of the tablet can be measured by a tester such as the Erweka® Model TBH 28. The tablet is stood on end and the machine tip moves to the tablet along an axial path. The force to break the tablet in two is normally recorded in newtons (N). Good tablets normally have strengths in the range of 8.896×10^3 to 4.448×10^4 N.

EXAMPLE 1

The following ingredients were weighed out and milled for 1 min in a Tekmar® A-10 analytical laboratory mill. The premix was passed through a 50 mesh screen and blended well. A 15 g tablet, 4.34 cm in diameter, was made with a hand-operated hydraulic press at a pressure of 525 kg/cm^2.

Ingredient	Concentration, Weight %
Thifensulfuron methyl	55.3
Citric Acid	10.0
Sodium Bicarbonate	25.4
Lomar PWA® (ammonium salt of naphthalene sulfonic acid-formaldehyde condensate)	5.7
Polyplasdone XL-100® (polyvinylpolypyrrolidone)	1.22
Monawet MB-100® (sodium diisobutyl sulfosuccinate)	1.05
Magnesium Oxide	1.33

The fresh tablet took 2 min and 23 sec to dissolve in 25°C water with only a trace of solids on the screens. A second 15 g tablet was allowed to sit at room temperature for 3 days to allow the water in it to diffuse into the internal desiccant (MgO). The tablet was sealed in a tight jar and aged at 45°C for 3 weeks. This accelerated aging simulates about two years of storage at ambient conditions. After aging, the tablet took 3 min and 10 sec to dissolve in 25°C water. The wet screens had only a trace of solids on them.

EXAMPLE 2

The following ingredients were milled and tableted as in Example 1.

Ingredient	Concentration, Weight %
Thifensulfuron methyl	52.7
Citric Acid	9.5
Sodium Bicarbonate	24.2
Lomar PWA® (ammonium salt of naphthalene sulfonic acid-formaldehyde condensate)	5.45
Polyplasdone XL-100® (polyvinylpolypyrrolidone)	1.15
Monawet MB-100® (sodium diisobutyl sulfosuccinate)	1.00
Molecular Sieves	6.00

The fresh tablet took 2 min and 50 s to break-up in 25°C water. There was only a trace of solids on the screens. The second tablet was aged as in Example 1. After aging, the tablet took 2 min and 51 s to break-up. There was only a trace of solids on the wet screens.

EXAMPLES 3 TO 19

In the same manner employed for Example 1, tablets can be prepared using the active ingredients in the first column of Table 2 with one or more of the desiccants listed in the second and third columns, except that when the base employed is potassium carbonate or bicarbonate, the desiccant(s) employed therewith are to be selected solely from Column A.

TABLE 2

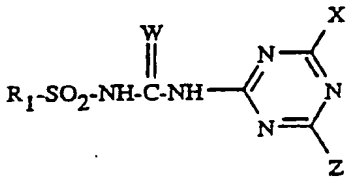
Active Ingredient	Desiccant	
	Column (A)	Column (B)
3) hexazinone	selected from the group, CaO, MgO, B_2O_3, $CaSO_4$, NaOAc, $MgSO_4$, Na_2SO_4, $CaCl_2$, and $ZnSO_4$	selected from the group highly dispersed silicilic acids such as silica gel, aluminum oxide, clays such as montmorillonite, and amorphous alumino-silicates such as molecular sieves and zeolites
4) 2,4-D		
5) chlorsulfuron		
6) sulfometuron methyl		
7) chlorimuron ethyl		
8) metsulfuron methyl		
9) ethametsulfuron methyl		
10) tribenuron ethyl		
11) bensulfuron methyl		
12) primisulfuron		
13) methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-6-(trifluoro-methyl)-3-pyridinecarboxylate		
14) 2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzenesulfonamide		
15) ethyl 5-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-1-methyl-1*H*-pyrazole-4-carboxylate		
16) *N*-[[(4,6-dimethoxy-2-pyrimidinylamino]-carbonyl]-3-(ethylsulfonyl)-2-pyridine-sulfonamide		
17) 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl]-*N*,*N*-dimethyl-3-pyridinecarboxamide		
18) methyl 2-[[[[[(4-(dimethylamino)-6-(2,2,2-trifluoroethoxy)-1,3,5-triazin-2-yl]amino]-carbonyl]sulfonyl]-3-methylbenzoate		
19) sodium 2-chloro-6-[(4,6-dimethoxy-2-pyrimidinyl)thio]benzoate		

EXAMPLES 20 TO 37

By the general procedure of Example 1, tablet formulations can be made whereby the active ingredient pesticide is as described hereafter and the delivery system with its characteristic internal desiccant is as defined herein.

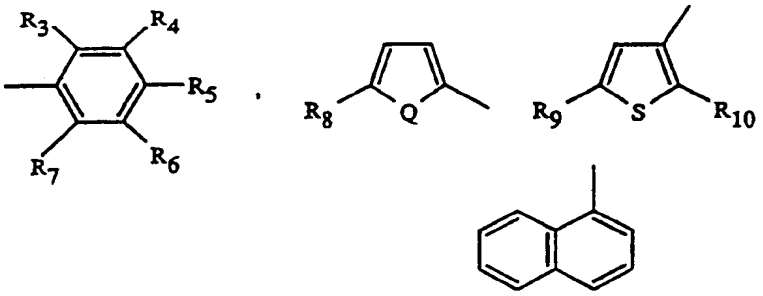
EXAMPLE 20

The pesticide, described in more detail in U.S. 4,127,405, is a compound of the formula:



wherein

R_1 is



R_3 and R_6 are independently hydrogen, fluorine, chlorine, bromine, iodine, alkyl of 1-4 carbon atoms, alkoxy of 1-4 carbon atoms, nitro, trifluoromethyl, cyano, $CH_3S(O)_n$- or $CH_3CH_2S(O)_n$-;

R_4 is hydrogen, fluorine, chlorine, bromine or methyl;

R_5 is hydrogen, fluorine, chlorine, bromine, methyl or methoxy;

R_7 is hydrogen, fluorine, chlorine, bromine, alkyl of 1-2 carbon atoms or alkoxy of 1-2 carbon atoms;

R_8 is hydrogen, methyl, chlorine or bromine;

R_9 and R_{10} are independently hydrogen, methyl, chlorine or bromine;

W and Q are independently oxygen or sulfur;

n is 0, 1 or 2;

X is hydrogen, chlorine, bromine, methyl, ethyl, alkoxy of 1-3 carbon atoms, trifluoromethyl, CH_3S- or CH_3OCH_2-; and

Z is methyl or methoxy, or their agriculturally suitable salts.

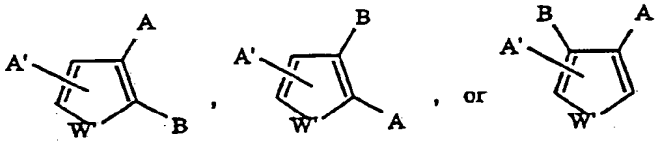
EXAMPLE 21

The pesticide, described in more detail in U.S. 4,394,506, is a compound of the formula:

N-(heterocyclicaminocarbonyl)arylsulfonamides in which the aryl radical is substituted in the 2-position by a carboxy radical, ester, thioester, or amide thereof; e.g., *N*-[(4,6-dimethylpyrimidin-2yl)aminocarbonyl]-methoxycarbonyl]benzenesulfonamide or *N*-[(4,6-dimethoxy-1,3,5-triazin-2-yl)amino-carbonyl]-2-methoxycarbonylbenzenesulfonamide.

EXAMPLE 22

The pesticide, described in more detail in U.S. 4,481,029, is a compound of the formula:



wherein

W' is O or S;

A' is H, Cl, Br, C_1-C_4 alkyl, OCH_3, NO_2 or CF_3;

A is $-\overset{O}{\overset{\|}{C}}-Q-R^{I}$ or $-\overset{T}{\overset{\|}{C}}-R^{II}$ where

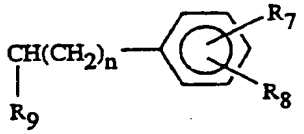
Q is O, S or $-\overset{R_4}{\overset{|}{N}}-$;

T is O or $=N-OR^{III}$

where

R^{III} is H, C_1-C_4 alkyl or C_3-C_4 alkenyl; when Q is O or S then

R^I is C_1-C_6 alkyl C_3-C_6 alkenyl; C_3-C_6 alkynyl; C_2-C_6 alkyl substituted with 1-3 Cl, F or Br, or one of CN or OCH_3; C_3-C_6 alkenyl substituted with 1-3 Cl; C_3-C_6 alkynyl substituted with Cl; C_5-C_6 cycloalkyl; cyclohexenyl; cyclohexyl substituted with 1-3 CH_3; C_4-C_7 cycloalkylalkyl or

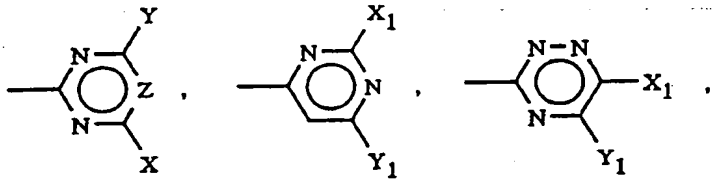


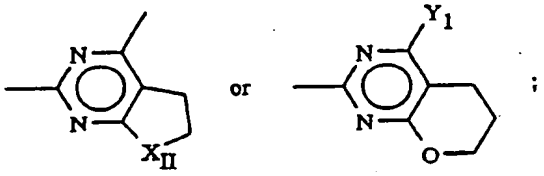
where

R_7 and R_8 are independently H, Cl, CH_3 or OCH_3;

n is 0 or 1; and

R_9 is H or CH_3;

R_1 is  ,

 ;

where

Z is N, CH or C-F;

X=H, Cl, $-CH_3$, $-OCH_3$ or $-OCH_2CH_3$;

Y=H, Cl, C_1-C_4 substituted alkyl;

with the proviso that when X and Y are both H, then

R^I and R^{II} are less than 5 carbons;

X_1=H, Cl, OCH_3, OCH_2CH_3 or CH_3;

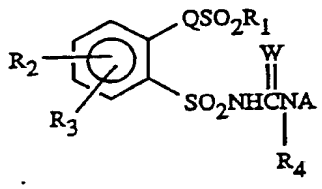
Y_1=H, OCH_3 or CH_3; and

X_{III}=O or CH_2 and further provided that when A contains greater than 5 carbon atoms, then Y contains ≤4 carbon atoms,and their agriculturally suitable salts;

all other substituents being as defined in U.S. 4,481,029.

EXAMPLE 23

The pesticide, described in more detail in U.S. 4,435,205, is a compound of the formula:

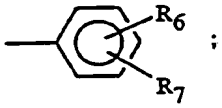


where

W is O or S;

Q is O or NR_5;

R_1 is C_1-C_4 alkyl, C_1-C_4 alkyl substituted with 1-3 atoms of F, Cl or Br, $CH_2CH_2OCH_3$, $CH_2CH_2CH_2OCH_3$ or



;

R_2 is H, F, Cl, Br, OCH_3, NO_2, CF_3 or C_1-C_2 alkyl;

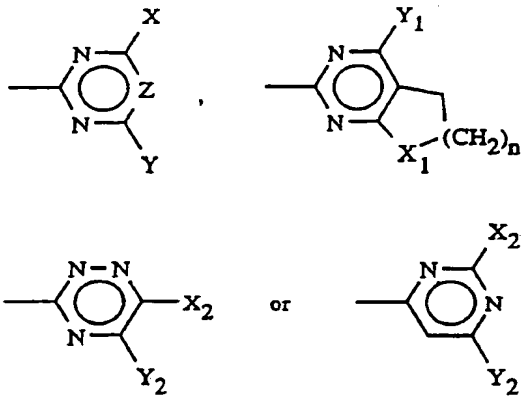
R_3 is H, F, Cl, Br or CH_3;

R_4 is H, CH_3 or OCH_3;

R_5 is C_1-C_4 alkyl;

R_6 and R_7 are independently H, F, Cl, Br, CH_3, CF_3, NO_2 or OCH_3;

A is



X is NH_2, $N(CH_3)_2$, $NHCH_3$, C_1-C_4 alkyl, C_1-C_4 alkyl substituted with 1-3 atoms of F, Cl or Br, CH_2OCH_3, $CH_2OCH_2CH_3$, C_1-C_4 alkoxy, C_1-C_2 alkylthio, C_3-C_4 alkenyloxy, C_3-C_4 alkynyloxy, $OCH_2CH_2OCH_3$ or C_2-C_4 alkoxy substituted with 1-3 atoms of F, Cl or Br;

n is 1 or 2;

Y is H, CH_3, OCH_3 or Cl;

X_1 is O or CH_2;

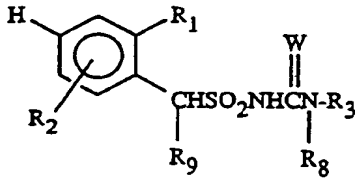
Y_1 is H, CH_3, OCH_3 or Cl;

X_2 and Y_2 are independently CH_3 or OCH_3; and

Z is CH, N, CCH_3, CBr, CCl, CF, CI, CC_2H_5, CCH_2CH_2Cl or $CCH_2CH{=}CH_2$.

EXAMPLE 24

The pesticide, described in more detail in U.S. 4,420,325, is a compound of the formula:



wherein

R_1 is F, Cl, Br, CF_3, C_1-C_3 alkoxy, C_1-C_3 alkyl, NO_2, CO_2R_4, SO_2R_5, $SO_2NR_6R_7$, $SO_2N(OCH_3)CH_3$, $SO_2OCH_2CF_3$, OSO_2R_5 or CH_2L;

L is $SO_2NR_6R_7$, OCH_3, OC_2H_5, CO_2H_5, CO_2CH_3 or $CO_2C_2H_5$;

R_2 is H, Cl, Br, F, CF_3 or OCH_3;

R_4 is C_1-C_3 alkyl, $CH_2CH{=}CH_2$, CH_2CH_2Cl or $CH_2CH_2OCH_3$;

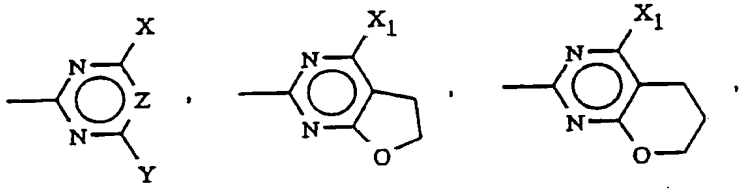
R_5 is C_1-C_3 alkyl or CF_3;

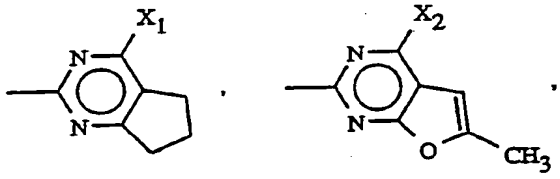
R_6 and R_7 are independently C_1-C_3 alkyl;

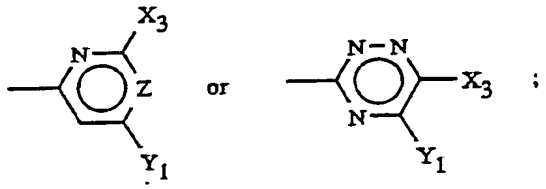
R_8 is H or CH_3;

R_9 is H or C_1-C_3 alkyl;

R_3 is







W is O or S;

X is CH_3, OCH_3 or Cl;

Y is CH_3, C_2H_5, OCH_3, OC_2H_5, CH_2OCH_3, NH_2, $NHCH_3$ or $N(CH_3)_2$;

Z is CH or N;

X_1 is H, Cl, CH_3, OCH_3 or OC_2H_5;

X_2 is CH_3, C_2H_5, OCH_3 or OC_2H_5;

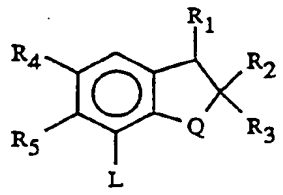
X_3 is CH_3 or OCH_3; and

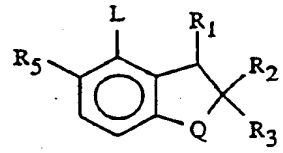
Y_1 is CH_3 or OCH_3;

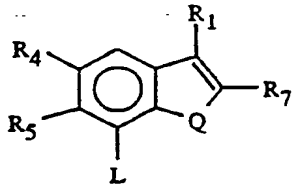
and their agriculturally suitable salts.

EXAMPLE 25

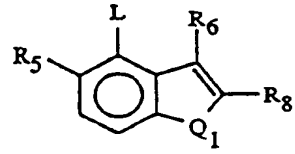
The pesticide, described in more detail in U.S. 4,514,211, is a compound of the formula:







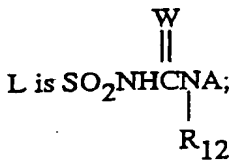
, or



wherein

Q is O, S, SO or SO_2;

Q_1 is O, S or SO_2;



L is SO_2NHCNA;

R_{12}

R_1 is H or C_1-C_4 alkyl;

R_2 is H or C_1-C_4 alkyl;

R_3 is H or CH_3;

R_4 is H, Cl, CH_3, CF_3, OCH_3, Br, F, SCH_3 or OCF_2H;

R_5 is H, CH_3, OCH_3, Cl, Br, NO_2, CO_2R_7, SO_2R_8, OSO_2R_9, $SO_2NR_{10}R_{11}$, F, CF_3, SCH_3, OCF_2H or $SO_2N(OCH_3)CH_3$;

R_6 is H, Cl, Br or C_1-C_4 alkyl;

R_6' is H, CH_3, Cl or Br;

R_7 is C_1-C_3 alkyl, $CH_2CH=CH_2$, $CH_2CH_2OCH_3$ or CH_2CH_2Cl;

R_8 is C_1-C_3 alkyl;

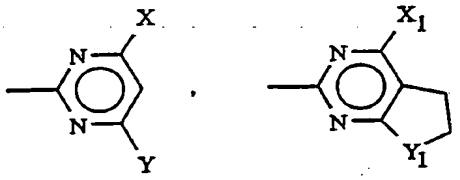
R_9 is C_1-C_3 alkyl or CF_3;

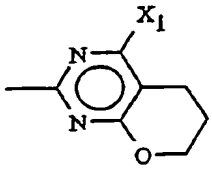
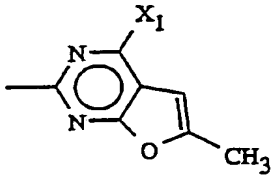
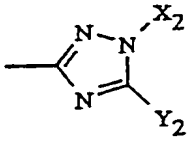
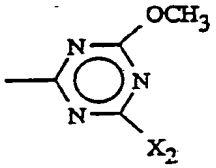
R_{10} and R_{11} are independently C_1-C_2 alkyl;

R_{12} is H or CH_3;

W is O or S;

A is






or

;

X is H, CH_3, OCH_3, Cl. F. OCF_2H or SCF_2H;

Y is CH_3, OCH_3, OC_2H_5, CH_2OCH_3, NH_2, $NHCH_3$, $N(CH_3)_2$, $CH(OCH_3)_2$, $CH(OCH_2CH_3)_2$, C_2H_5, CF_3, $CH_2=CHCH_2O$, $CH\equiv CCH_2O$. CF_3CH_2O, OCH_2CH_2Cl, OCH_2CH_2Br, OCH_2CH_2F,

CN, $CH_2OCH_2CH_3$, $OCH_2CH_2OCH_3$ or GCF_2T wherein G is O or S and T is H, CHClF, CHBrF, CF_2H or $CHFCF_3$;

Z is CH, N, CCH_3, CC_2H_5, CCl or CBr;

Y_1 is O or CH_2;

X_1 is CH_3, OCH_3, OC_2H_5 or OCF_2H;

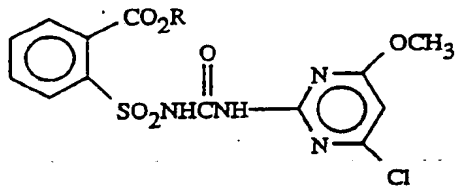
X_2 is CH_3, C_2H_5 or CH_2CF_3;

Y_2 is C_2H_5, CH_3, OCH_3, OC_2H_5, SCH_3 or SC_2H_5; and

X_3 is CH_3 or OCH_3.

EXAMPLE 26

The pesticide, described in more detail in U.S. 4,547,215, is a compound of the formula:



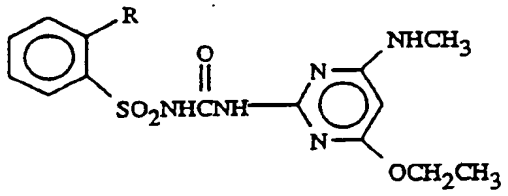
wherein

R is C_2H_5 or $CH(CH_3)_2$;

and their agriculturally suitable salts.

EXAMPLE 27

The pesticide, described in more detail in U.S. 4,548,638, is a compound of the formula:

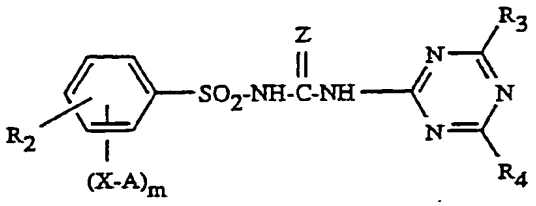


wherein

R is CO_2CH_3, $CO_2CH_2CH_3$, $CO_2CH_2CH_2CH_3$, $CO_2CH_2CH=CH_2$, $CO_2CH(CH_3)$, $CO_2CH_2CH_2Cl$, $SO_2N(CH_3)_2$ or OSO_2CH_3.

EXAMPLE 28

The pesticide, described in more detail in U.S. 4,479,821, is a compound of the formula:



wherein

A is a C_1-C_6 alkyl radical which is substituted by C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl or C_1-C_4 alkylsulfonyl;

X is oxygen, sulfur, a sulfinyl or sulfonyl bridge;

Z is oxygen or sulfur;

m is 1 or 2;

R_2 is hydrogen, halogen, C_1-C_5 alkyl, C_2-C_5 alkenyl, C_1-C_4 haloalkyl, or a radical -Y-R_5, -$COOR_6$, -NO_2 or -CO-NR_7R_8;

R_3 and R_4, each independently of the other, are hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl, halogen or alkoxy-alkyl of at most 4 carbon atoms;

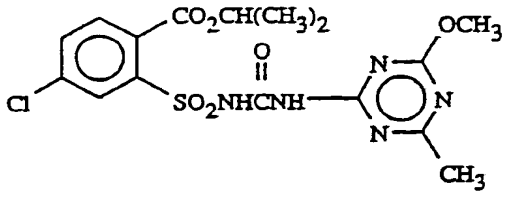
R_5 and R_6, each independently of the other, are C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_6 alkynyl;

R_7 and R_8, each independently of the other, are hydrogen, C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_6 alkynyl; and

Y is oxygen, sulfur, a sulfinyl or sulfonyl bridge, and salts of these compounds.

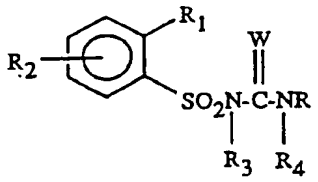
EXAMPLE 29

The pesticide, described in more detail in U.S. 4,566,898, is a compound of the formula:



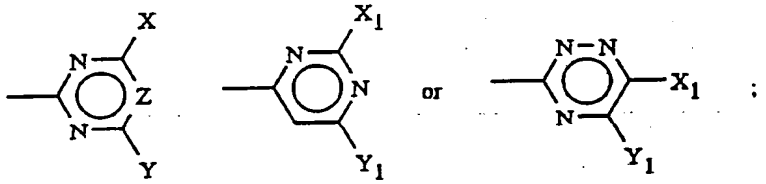
EXAMPLE 30

The pesticide, described in more detail in U.S. 4,435,206, is a compound of the formula:



wherein

R is



R_1 is H, Cl, Br, F, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, NO_2, CF_3, $COOR_5$ or $SO_2NR_6R_7$;

R_2 is H, Cl, Br or CH_3;

R_3 and R_4 are independently H or CH_3;

R_5 is C_1-C_6 alkyl, C_3-C_6 alkenyl, $CH_2CH_2OCH_3$, $CH_2CH_2OCH_2CH_3$, $CH_2CH_2CH_2OCH_3$ or CH_2CH_2Cl;

R_6 and R_7 are independently CH_3 or CH_3CH_2;

W is oxygen or sulfur;

X is CH_3 $-OCH_3$ or $-OCH_2CH_3$;

Y is H, Cl, CH_3, CF_3, $-NHCH_3$, $-N(CH_3)_2$-, $-CH_2OR_8$, $-CH_2CH_2OR_8$, $-OCH_2CF_3$ or VR_6;

Z is CH or N;

V is oxygen or sulfur;

R_8 is CH_3, CH_3CH_2-, $CH_2CO_2R_8$, $-CH_2CH_2OR^6$, $C(CH_3)HCO_2R_8$ or $CH_2CH_2CO_2R_8$;

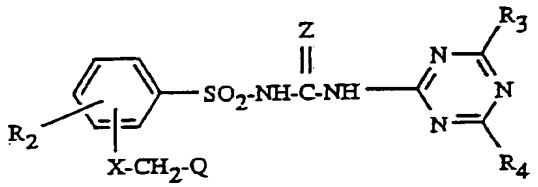
Y_1 is H, CH_3 or OCH_3; and

X_1 is H, Cl, -OCH_3, -OCH_2CH_3 or CH_3;

and agricultural salts thereof.

EXAMPLE 31

The pesticide, described in more detail in U.S. 4,514,212, is a compound of the formula:



and the salts thereof with amines, alkali metal or alkaline earth metal bases or with quaternary ammonium bases wherein:

Q is fluorine, fluoromethyl, chloromethyl, trichloromethyl, 1,2-dichloroethyl, 1,2-dibromoethyl, 1,2-dichloropropyl, 1,2-dibromopropyl, 1,2-dibromoisobutyl, 1,2-dichloro-1-methyl-ethyl or 1,2-dibromo-1-methylethyl;

X is oxygen, sulfur, a sulfinyl or sulfonyl bridge;

Z is oxygen or sulfur;

R_2 is hydrogen, halogen, C_1-C_5 alkyl, C_2-C_5 alkenyl, C_1-C_4 haloalkyl, or a radical -Y-R_5, -$COOR_6$, -NO_2 or -CO-NR_7-R_8;

R_3 and R_4, each independently of the other, are hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 haloalkyl, halogen or alkoxyalkyl of at most 4 carbon atoms;

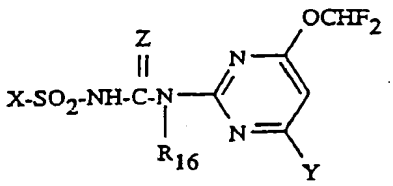
R_5 and R_6, each independently of the other, are C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_6 alkynyl;

R_7 and R_8, each independently of the other, are hydrogen, C_1-C_5 alkyl, C_2-C_5 alkenyl or C_2-C_6 alkynyl; and

Y is oxygen, sulfur, a sulfinyl or sulfonyl bridge.

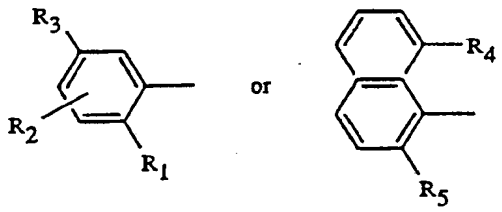
EXAMPLE 32

The pesticide, described in more detail in U.S. 4,478,635, is a compound of the formula:



wherein

X is a radical of the formula:



Y is C_1-C_3 alkyl, C_1-C_3 haloalkyl, C_1-C_3 alkoxy, C_1-C_3 haloalkoxy, C_2-C_3 alkoxyalkyl, C_1-C_3 alkylthio, halogen or $-NR_{16}R_{17}$;

Z is oxygen or sulfur;

R_1 is hydrogen, halogen, cyano, nitro, C_1-C_4 haloalkyl, C_1-C_4 alkyl, C_1-C_4 alkoxy, $-CO-R_6$, $-NR_7R_8$, $-S(O)_m-C_1-C_4$ alkyl or $-SO_2R_9$;

R_2 is hydrogen, fluorine, chlorine, bromine, nitro, trifluoromethyl, $-NR_{20}R_{21}$, methyl, ethyl, methoxy, ethoxy or $-S(O)_m-C_1-C_4$ alkyl;

R_3 is hydrogen, fluorine, chlorine, bromine, amino, nitro or methoxy;

R_6 is hydrogen, C_1-C_4 alkyl, C_1-C_3 alkenyloxy, C_3-C_5 alkynyloxy, C_1-C_4 haloalkyl, C_1-C_5 alkylthio, phenoxy, benzyloxy, $-NR_{10}R_{11}$ or C_1-C_5 alkoxy which is unsubstituted or substituted by 1 to 3 halogen atoms or C_1-C_3 alkoxy;

R_7 is hydrogen, methoxy, ethoxy, C_1-C_4 alkyl or $-CO-R_{12}$;

R_8 is hydrogen or $-CO-R_{12}$;

R_9 is an $-O-R_{13}$ or $-NR_{14}R_{15}$ group;

R_{11} is C_1-C_4 alkyl which is unsubstituted or substituted by 1 to 3 halogen atoms, or is phenyl or benzyl;

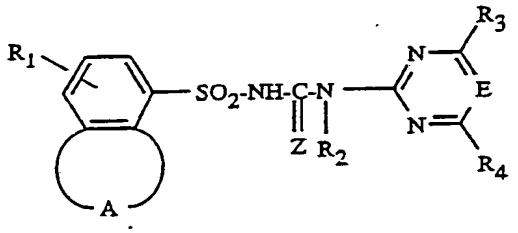
R_{12} is hydrogen, C_1-C_4 alkyl or C_1-C_4 alkoxy; and

m is 0, 1 or 2;

and R_4 has the same meaning as R_2; R_5 has the same meaning as R_1; R_{10}, R_{11}, R_{14} and R_{20} each have the same meaning as R_7; and R_{12}, R_{15}, R_{16}, R_{17} and R_{21} each have the same meaning as R_8.

EXAMPLE 33

The pesticide, described in more detail in U.S. 4,634,465, is a compound of the formula:



wherein

Z is oxygen or sulfur;

E is nitrogen or =C-;

R_1 is hydrogen, halogen, nitro, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 alkoxycarbonyl, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl or C_2-C_5 alkoxyalkoxy;

R_2 is hydrogen, C_1-C_4 alkyl or C_1-C_3 alkoxy;

R_3 and R_4, each independently of the other, are hydrogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkoxy, C_1-C_4 haloalkylthio, C_1-C_4 alkylthio, halogen, C_2-C_5 alkoxyalkyl, C_2-C_5 alkoxyalkoxy or $-NR_5R_6$, wherein R_5 and R_4 are hydrogen or C_1-C_4 alkyl; and

A is an unsubstituted or substituted bridge of 3 or 4 atoms which contains 1 or 2 oxygen, sulfur or nitrogen atoms and, together with the linking carbon atom, forms a non-aromatic 5- or 6-membered heterocyclic ring system, with the proviso that two oxygen atoms are separated by at least one carbon atom and that oxygen and sulfur atoms are only linked to each other if the sulfur atom takes the form of the -SO- or $-SO_2-$ group.

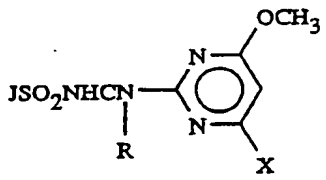
EXAMPLE 34

The pesticide, described in more detail in EPA-202,830, is:

2-[[*N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-*N*-methylamino-carbonyl]aminosulfonyl]benzoic acid, methyl ester.

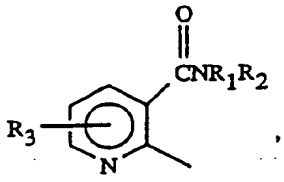
EXAMPLE 35

The pesticide, described in more detail in EPA-237,292, is a compound of the formula:

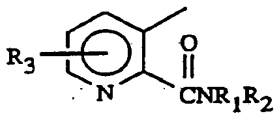


wherein

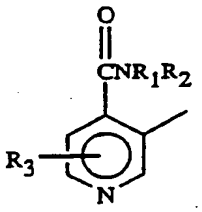
J is



J-1

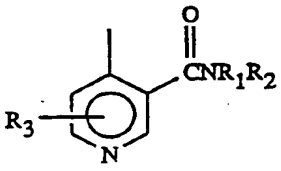


J-2



J-3

or



J-4

;

R is H or CH_3;

R_1 is H or C_1-C_3 alkyl;

R_2 is C_1-C_3 alkyl or C_1-C_2 alkoxy; or

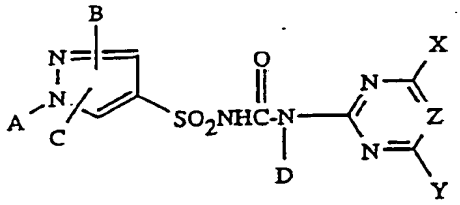
R_1 and R_2 may be taken together to form -(CH_2)n-, wherein n is 2, 3 or 4;

R_3 is H, Cl, F, Br, CH_3, CF_3, OCH_3 or COF_2H; and

X is CH_3, CH_2F, CH_2CH_3, OCH_3, OCH_2CH_3, Cl, OCF_2H or CH_2OCH_3.

EXAMPLE 36

The pesticide, described in more detail in EPA-87,780, is a compound of the formula:



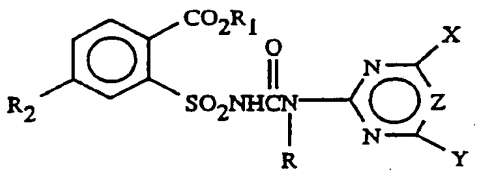
wherein

A represents a hydrogen atom, a C_1-C_8 alkyl group or a phenyl group which may be substituted with C_1-C_8 alkyl groups, halogen atoms or nitro groups; B and C represent independently hydrogen atoms, halogen atoms, nitro groups, C_1-C_8 alkyl groups, arylalkyl groups, C_1-C_8 alkoxy groups; haloalkyl groups, $-CO_2R$ [where R is a hydrogen atom, a C_1-C_8 alkyl group, an allyl group or a propargyl group), $-CONR_1R_2$ (where R_1 is a hydrogen atom, a C_1-C_8 alkyl group or a phenyl group, R_2 is a hydrogen atom or a C_1-C_8 alkyl group, or R_1 and R_2 taken together may represent $-(CH_2)_m-$ (m is 4, 5 or 6), $-CH_2CH_2OCH_2CH_2-$, or $-CH_2CH_2N(CH_3)CH_2CH_2-$], $-S(O)_nR_3$ (where R_3 is a C_1-C_8 alkyl group, a phenyl group or an arylalkyl group and n is 0, 1 or 2), $-SO_2NR_4R_5$ [where R_4 is a C_1-C_8 alkyl group, R_5 is a hydrogen atom or a C_1-C_8 alkyl group, or R_4 and R_5 taken together may represent $-(CH_2)_p-$ (p is 4, 5 or 6), $-CH_2CH_2OCH_2CH_2-$ or $-CH_2CH_2N(CH_3)CH_2CH_2-$] or a phenyl group which may be substituted with C_1-C_8 alkyl groups, halogen atoms or nitro groups, D represents a hydrogen atom or a C_1-C_8 alkyl group; X and Y represent independently hydrogen atoms, halogen atoms, C_1-C_8 alkyl groups, C_1-C_8 alkoxy groups, C_1-C_8 alkoxyalkyl groups, $-CF_3$ groups, C_1-C_8 haloalkoxy groups, alkylamino groups, dialkylamino groups, $-OCHCO_2R_7$ (where R_6 and R_7 each represent hydrogen atoms or C_1-C_8 alkyl groups) or either X or Y may form a five-membered ring containing an oxygen atom together with X; and X represents a nitrogen atom or C-R_8 (where R_8 represents a hydrogen atom, a haloalkyl group or may

form a five-membered ring containing an oxygen atom together with X or Y).

EXAMPLE 37

The pesticide, described in more detail in U.S. 4,710,221, is a compound of the formula:



wherein

R is H or CH_3;

R_1 is C_1-C_3 alkyl, C_3-C_4 alkoxyalkyl, C_2-C_4 haloalkyl, C_3-C_4 alkenyl or C_3-C_4 alkynyl;

R_2 is C_2-C_6 alkoxy, C_3-C_6 cycloalkoxy, C_4-C_6 cycloalkylalkoxy, C_1-C_6 haloalkoxy, C_2-C_6 alkenyloxy, C_2-C_6 haloalkenyloxy, C_3-C_6 alkynyloxy, C_3-C_6 haloalkynyloxy, C_2-C_4 alkoxyalkoxy, C_2-C_4 haloalkoxyalkoxy, C_2-C_4 alkylthioalkoxy, C_2-C_4 haloalkylthio-alkoxy, C_2-C_4 alkylsulfinylalkoxy, C_2-C_4 haloalkylsulfinylalkoxy, C_2-C_4 alkylsulfonylalkoxy, C_2-C_4 haloalkylsulfonylalkoxy, C_2-C_4 cyanoalkoxy, $OCH_2C(O)CH_3$, $OCH_2CH_2C(O)CH_3$, C_2-C_4 aminoalkoxy, C_1-C_8 alkylthio, C_3-C_6 cycloalkylthio, C_4-C_6 cycloalkylalkylthio, C_1-C_8 haloalkylthio, C_2-C_6 alkenylthio, C_2-C_6 haloalkenylthio, C_3-C_6 alkynylthio, C_3-C_6 haloalkynylthio, C_2-C_4 alkoxyalkylthio, C_2-C_4 haloalkoxyalkylthio, C_2-C_4 alkylthio-alkylthio, C_2-C_4 haloalkylthioalkylthio, C_2-C_4 cyanoalkylthio, $SCH_2C(O)CH_3$, $SCH_2CH_2C(O)CH_3$, C_2-C_4 aminoalkylthio, SC_6H_5, $SCH_2C_6H_5$, C_1-C_8 alkylsulfinyl, C_3-C_6 cycloalkylsulfinyl, C_4-C_6 cycloalkylalkylsulfinyl, C_1-C_8 haloalkylsulfinyl, C_2-C_6 alkenyl-sulfinyl, C_2-C_6 haloalkenylsulfinyl, C_3-C_6 alkynylsulfinyl, C_3-C_6 haloalkynylsulfinyl, C_2-C_4 alkoxyalkylsulfinyl, C_2-C_4 haloalkoxy-alkylsulfinyl, C_2-C_4 cyanoalkylsulfinyl, $S(O)CH_2C(O)CH_3$, $S(O)CH_2CH_2C(O)CH_3$, C_2-C_4 aminoalkylsulfinyl, C_2-C_8 alkylsulfonyl, C_3-C_6 cycloalkylsulfonyl, C_4-C_6 cycloalkylalkyl-

sulfonyl, C_1-C_8 haloalkylsulfonyl, C_2-C_6 alkenylsulfonyl, C_2-C_6 haloalkenylsulfonyl, C_3-C_6 alkynylsulfonyl, C_3-C_6 haloalkynylsulfonyl, C_2-C_4 alkoxyalkylsulfonyl, C_2-C_4 haloalkoxyalkylsulfonyl, C_2-C_4 cyanoalkylsulfonyl, $SO_2CH_2C(O)CH_3$, $SO_2CH_2CH_2C(O)CH_3$, C_2-C_4 aminoalkylsulfonyl, CH_2F, CH_2Cl, $CHCl_2$, CH_2Br, $CHBr_2$, C_2-C_6 alkyl substituted with 1-3 atoms of F, Cl or Br, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl, $C{\equiv}CH$, C_2-C_6 haloalkynyl, $OC(O)C_1$-C_4 alkyl, $CH_2C(O)NR_aR_b$, $NHCH_3$, NR_bR_c or C_1-C_4 alkyl substituted with C_1-C_4 alkoxy, C_3-C_4 cycloalkoxy, cyclopropylmethoxy, C_1-C_4 haloalkoxy, C_2-C_4 alkenyloxy, C_2-C_4 haloalkenyloxy, C_3-C_4 alkynyloxy, C_3-C_4 haloalkynyloxy, C_2-C_4 alkoxyalkoxy, C_2-C_4 aminoalkoxy, C_1-C_4 alkylcarbonyloxy, C_1-C_4 haloalkylcarbonyloxy, C_1-C_4 carbamoyloxy, C_1-C_4 alkoxycarbonyloxy, OH, $OP(O)(OC_1$-C_2 alkyl$)_2$, C_1-C_4 alkylsulfonyloxy, C_1-C_2 haloalkylsulfonyloxy, $OSi(CH_3)_3$, $OSi(CH_3)_2C(CH_3)_3$, C_1-C_4 alkylthio, C_3-C_4 cycloalkylthio, cyclopropylmethylthio, C_1-C_4 haloalkylthio, C_2-C_4 alkenylthio, C_2-C_4 haloalkenylthio, C_3-C_4 alkynylthio, C_3-C_4 haloalkynylthio, C_2-C_4 alkoxyalkylthio, C_2-C_4 aminoalkylthio, SH, $SP(O)(OC_1$-C_2 alkyl$)_2$, C_1-C_4 alkylsulfinyl, C_3-C_4 cycloalkylsulfonyl, cyclopropylmethylsulfinyl, C_1-C_4 haloalkylsulfinyl, C_2-C_4 alkenylsulfinyl, C_2-C_4 haloalkenylsulfinyl, C_3-C_4 alkynylsulfinyl, C_3-C_4 haloalkynylsulfinyl, C_2-C_4 alkoxyalkylsulfinyl, C_2-C_4 aminoalkylsulfinyl, C_1-C_4 alkylsulfonyl, C_3-C_4 cycloalkylsulfonyl, cyclopropylmethylsulfonyl, C_1-C_4 haloalkylsulfonyl, C_2-C_4 alkenylsulfonyl, C_2-C_4 haloalkenylsulfonyl, C_3-C_4 alkynylsulfonyl, C_3-C_4 haloalkynylsulfonyl, C_2-C_4 alkoxyalkylsulfonyl or C_2-C_4 aminoalkylsulfonyl;

R_a and R_b are independently H or C_1-C_3 alkyl;

R_c is C_2-C_4 alkyl, cyclopropylmethyl, C_2-C_4 cyanoalkyl, $CH_2C(O)CH_3$, $CH_2CH_2C(O)CH_3$, C_{10}-C_4 haloalkyl, C_3-C_4 alkenyl, C_3-C_4 haloalkenyl, C_3-C_4 alkynyl, C_3-C_4 haloalkynyl, C_1-C_4 alkyl substituted with C_1-C_4 alkoxy, C_1-C_4 alkylthio, C_1-C_4 alkylsulfinyl, C_1-C_4 alkylsulfonyl, OH, NH_2, $NHCH_3$ or $N(CH_3)_2$;

X is CH_3, OCH_3, OC_2H_5, Cl or Br;

Y is C_1-C_2 alkyl, C_1-C_2 alkoxy, OCH_2CH_2F, OCH_2CHF_2, OCH_2CF_3, $NHCH_3$ or $N(CH_3)_2$; and

Z is CH or N; and

their agriculturally suitable salts.

CLAIMS

What is claimed is:

1. A tablet formulation consisting essentially of by total weight of the formulated composition:

(i) about 0.1% to 75% of a pesticide;

(ii) about 25% to 99.9% of a delivery system characterized by a panel of components complementary to the pesticide of (i) having the following components:

(a) about 5% to 75% of a dibasic or tribasic organic carboxylic acid or a mixture thereof;

(b) about 5% to 75% of an ammonium, lithium, sodium or potassium carbonate or bicarbonate or a mixture thereof;

(c) about 0.5% to 20% of a dispersant;

(d) about 0.1% to 5% of water-insoluble cross-linked polyvinylpolypyrrolidone;

(e) about 0.1% to 5% of an anionic or nonionic wetting agent; and

(f) about 1% to 20% of an internal desiccant being selected from the group:

(A) one or a mixture of desiccants that chemically bind water, and

(B) one or a mixture of desiccants that physically adsorb water;

the desiccant being (A) when (b) is potassium carbonate or potassium bicarbonate.

2. A tablet formulation according to Claim 1 wherein (b) is an ammonium, sodium or lithium carbonate or bicarbonate or mixture thereof, and the internal desiccant is selected from (A), (B) and a mixture of (A) and (B).

3. A tablet formulation according to Claim 1 wherein (b) is potassium carbonate or bicarbonate or mixture thereof, and the internal desiccant is (A).

4. A tablet formulation according to Claim1 in the form of a tablet.

5. A tablet formulation according to Claim2 in the form of a tablet.

6. A tablet formulation according to Claim3 in the form of a tablet.

7. A tablet formulation according to any one of Claims 1 to 6 wherein the pesticide is a sulfonylurea herbicide selected from the group consisting of chlorsulfuron, sulfometuron methyl, chlorimuron ethyl, metsulfuron methyl, ethametsulfuron methyl, thifensulfuron methyl, tribenuron ethyl, bensulfuron methyl, primisulfuron, methyl 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-

carbonyl]amino]sulfonyl]-6-(trifluoro-methyl)-3-pyridinecarboxylate, 2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzenesulfonamide, ethyl 5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-1-methyl-1*H*-pyrazole-4-carboxylate, *N*-[[(4,6-dimethoxy-2-pyrimidinylamino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide, 2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-*N*,*N*-dimethyl-3-pyridinecarboxamide, and methyl 2-[[[[[4-(dimethylamino)-6-(2,2,2-trifluoro-ethoxy)-1,3,5-triazin-2-yl]amino]carbonyl]sulfonyl]-3-methylbenzoate.

8. A tablet formulation according to Claim 7 wherein the pesticide is a sulfonylurea herbicide selected from the group consisting of thifensulfuron methyl, tribenuron ethyl, and bensulfuron methyl.

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A01N25/34; A01N47/36; A01N43/64; A01N39/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	EP,A,0 391 851 (CIBA-GEIGY) 10 October 1990 see column 1, line 1 - line 24 see column 2, line 1 - line 20 see column 2, line 36 - column 4, line 16 see column 5, line 2 - column 9, line 55	1,2,4,5, 7,8
Y	& CA,A,2 013 918 cited in the application ---	3,6
Y	PATENT ABSTRACTS OF JAPAN vol. 9, no. 1 (C-259)(1724) 5 January 1985 & JP,A,59 155 311 (NISSAN) 4 September 1984 see abstract --- -/--	3,6

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
18 MARCH 1993	20. 04. 93
International Searching Authority	**Signature of Authorized Officer**
EUR PEAN PATENT FFICE	LAMERS W.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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Y	GB,A,2 242 130 (INFOWISE) 25 September 1991 see page 4, line 2 - line 19 see page 6; example B see page 7, line 7 - line 12	1,2,4,5, 7,8
P,X	EP,A,0 488 660 (SUMITOMO CHEMICAL) 3 June 1992 see page 2, line 10 - page 7, line 5 see page 7, line 21 - line 24	1-8
A	EP,A,0 415 688 (AECI) 6 March 1991 see the whole document	1-8
A	EP,A,0 367 887 (CIBA-GEIGY) 16 May 1990 see the whole document	1-8
A	US,A,4 180 467 (J.B.BARTH) 25 December 1979 see column 1, line 11 - line 26 see column 1, line 65 - column 2, line 22	1-8
A	DE,A,2 710 107 (HOYER) 14 September 1978 see page 2; claims 9,10 see page 8, paragraph 3 - page 9, paragraph 3	1-8

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9211305
SA 68875

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent ffice EDP file on
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US-A-4180467	25-12-79	None		
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For more details about this annex : see ficial Journal of the European Patent ffice, No. 12/82